

# Radiolysis of Liquid Propane: Radical Reactions<sup>1</sup>

By R. D. KOOB<sup>2</sup> AND LARRY KEVAN

Dept. of Chemistry, University of Kansas, Lawrence, Kansas 66044

The radical reactions in the liquid phase  $\gamma$ -radiolysis of propane have been studied from  $-130$  to  $35^\circ\text{C}$  and compared with the gas-phase radiolysis at  $35^\circ\text{C}$ . Oxygen was used as a scavenger to separate thermal radical yields, and effects of phase and temperature on the radical yields were assessed. The gas-liquid phase change (a) decreases total decomposition by about 14 %, (b) increases disproportionation/combination (D/C) ratios for all radicals by 30 %, and (c) decreases the isopropyl/n-propyl radical ratio. The decrease in liquid temperature (a) changes the predominant reaction of H atoms from abstraction from propane to addition to product propylene below  $-78^\circ\text{C}$  at doses of 1 Mrad, (b) increases the D/C ratios by 31 % and (c) decreases the isopropyl/n-propyl radical ratio. Dose effects were briefly studied; they are complex and cannot be explained by radical reactions alone.

Propane radiolysis has been studied in the gas phase, and the overall mechanism is understood in terms of radical, ionic and excited molecule reactions.<sup>3-8</sup> Radical yields and reactions have been studied by comparing product yields in the absence and presence of radical scavengers. Here we extend the study of radical reactions in irradiated propane to the liquid phase. Attention has been paid to the separation of phase and temperature effects. Specific phase effects are delineated by comparison of gas and liquid yields at constant temperature. The phase change lowers the average excitation energy of the propane species which decompose to radicals; it also affects the disproportionation-combination (D/C) ratio of propyl radicals. Temperature changes the predominant reaction of H atoms in the system, and also changes the D/C ratio of propyl radicals.

Radiation dose effects are qualitatively understood in the gas phase.<sup>7-9</sup> Additional data are given here for the liquid phase, but dose effects remain incompletely understood.

## EXPERIMENTAL

Phillips research-grade propane was purified chromatographically (impurity  $<2$  p.p.m.) and then thoroughly degassed by several freeze-pump-thaw cycles. The oxygen used as scavenger was obtained from Air Products. It was Extra Dry Grade (99.6 % pure), and was used without purification.

The components of the sample were condensed, in order of vapour pressure, into ampoules fabricated from 2 mm int. diam. Pyrex heavy-wall capillary tubing. The samples were then irradiated in a U.S. Nuclear GR9 Irradiator with a Co-60 source. The dose rate was determined by ferrous dosimetry to be 0.602 Mrad/h; monthly corrections for decay were made. Irradiations made at  $-78^\circ$  were done with the samples immersed in crushed dry ice. The  $-130^\circ\text{C}$  temperature was obtained by passing precooled air through the dewar containing the samples.

The dose to a ferrous sulphate solution was measured in ampoules identical to those used for the samples. This dose was corrected by the total mass-energy absorption coefficient of the sample to give the total dose to the sample. The stopping power factors in the total mass-energy absorption coefficients were calculated from the empirical equations of Bailey and Brown.<sup>10</sup>

Analysis was achieved with gas-liquid chromatography using thermal conductivity and flame ionization detectors. By employing a switching system which allowed the columns to be placed first in series and then in parallel, it was possible to obtain quantitative analysis of all hydrocarbon product peaks, with the exception of isobutane, using only one aliquot.<sup>11</sup> The isobutane n-butane ratio was obtained using a second aliquot on a separate column. The columns employed were: C<sub>4</sub>-C<sub>6</sub>, didecyl phthalate 10 % w/w on Chromosorb W (HMDS), 1/4 in x 25 ft; C<sub>1</sub>-C<sub>3</sub>, propylene carbonate 30 % w/w on alumina, 1/4 in x 50 ft; and i-C<sub>4</sub>/n-C<sub>4</sub>, propylene carbonate 10 % w/w on alumina, 1/4 in x 20 ft. The first two columns were maintained at 0°C and the third column was operated at room temperature.

## RESULTS

Oxygen can act as a free radical scavenger and as an electron trap. If O<sub>2</sub><sup>-</sup> were formed it would probably provide the major neutralization reaction for positive ions. If O<sub>2</sub><sup>-</sup> neutralization results in a different distribution of radicals than electron neutralization the interpretation of the free radical reactions would be complex. Other free radical scavengers which are not good electron traps such as butadiene and propylene have also been investigated. These scavengers give similar results to oxygen so we conclude that O<sub>2</sub><sup>-</sup> neutralization, if important, does not greatly change the radical distribution.

TABLE 1.—LOW CONVERSION (1 Mrad) 100 eV YIELDS (G) IN PROPANE RADIOLYSIS<sup>a</sup>

phase temperature additive	gas <sup>b</sup> 35°C none O <sub>2</sub>	liquid 35°C none O <sub>2</sub>	liquid -78°C none O <sub>2</sub>	liquid -130°C none O <sub>2</sub>
CH <sub>4</sub>	1.4 0.62	0.75 0.31	0.56 0.37	0.51 0.29
C <sub>2</sub> H <sub>4</sub>	1.0 0.88	0.66 0.51	0.57 0.48	0.48 0.34
C <sub>2</sub> H <sub>6</sub>	2.2 1.5	0.50 0.37	0.42 0.24	0.38 0.16
C <sub>3</sub> H <sub>2</sub>	0.31 0.31	0.09 0.09	0.06 0.05	0.07 0.04
C <sub>3</sub> H <sub>6</sub>	2.0 0.88	2.9 0.88	2.6 1.0	2.5 0.88
i-C <sub>4</sub> H <sub>10</sub>	1.4 <sup>c</sup> 0.0	0.8 <sup>c</sup> 0.0	0.3 <sup>c</sup> 0.0	0.14 0.0
n-C <sub>4</sub> H <sub>10</sub>	0.33 0.0	0.3 0.0	0.2 0.0	0.16 0.0
i-C <sub>5</sub> H <sub>12</sub>	0.29 0.0	0.13 0.0	0.15 0.0	0.07 0.0
n-C <sub>5</sub> H <sub>12</sub>	0.07 0.0	0.07 0.0	0.14 0.0	0.11 0.0
2,2-Me <sub>2</sub> C <sub>4</sub>	1.7 0.0	1.4 0.0	0.61 0.0	0.34 0.0
2-MeC <sub>5</sub>	0.48 0.0	0.85 0.0	1.14 0.0	0.58 0.0
n-C <sub>6</sub> H <sub>14</sub>	0.07 0.0	0.15 0.0	0.53 0.0	0.29 0.0
G(-C <sub>3</sub> H <sub>8</sub> ) <sup>d</sup>	12.1 2.9	10.4 1.6	9.3 1.6	6.4 1.6

<sup>a</sup> less than ±15 % deviation; <sup>b</sup> pressure; 1 atm; <sup>c</sup> approximate due to poor resolution; <sup>d</sup> based on carbon yields in products.

Oxygen was used as a thermal radical scavenger at a nominal concentration of >1 % in the liquid phase; this was sufficient to scavenge all radicals. Oxygen gave consistent scavenging results in gaseous and liquid propane over a wide temperature range. Nitric oxide did not prove satisfactory because it can participate in exothermic charge transfer reactions with propane. Scavengeable product yields (ΔG) are defined as the yield in the absence of scavenger minus the yield in the presence of scavenger. Except for radiation dose results the yields are usually reported at 1 Mrad dose. Separate dose-yield data show that 1 Mrad doses essentially correspond to initial yields. However, olefins can undergo H atom addition even at very low doses, and the scavengeable yields for olefins are lower limits. Table 1 compares the yields of products for scavenged and unscavenged samples in the gas at 35°C and in the liquid phase at 35, -78 and -130°C. All values are averages of three or more samples. Deviations are less than 15 %.

Our gas-phase data for unscavenged runs are in excellent agreement with that of Bone, Sieck and Futrell<sup>7,8</sup> with regard to fragmentation products. Combination products in our data appear in somewhat larger quantities. Agreement is also good for scavenged results except for methane which we find to be about 30 % lower. Bone *et al.* used a variety of scavengers but did not use oxygen; they consider their "best" scavenger to be butadiene. We have compared oxygen and butadiene as scavengers in the gas phase and find good agreement, although in our experiments

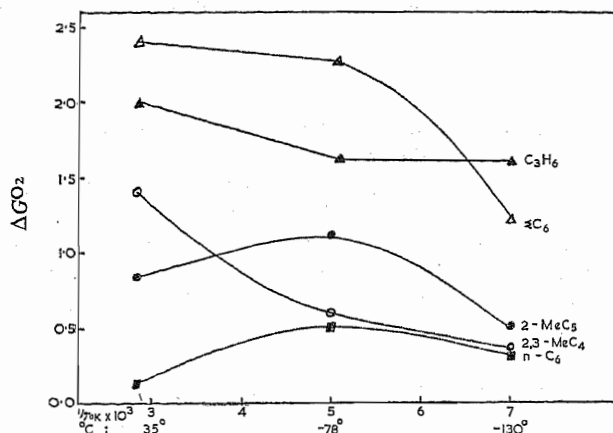


FIG. 1.—Radical yields  $\Delta G_{O_2}$  against reciprocal temperature ( $1/T$ ) for liquid propane  $\gamma$ -irradiated to 1.2 Mrad.

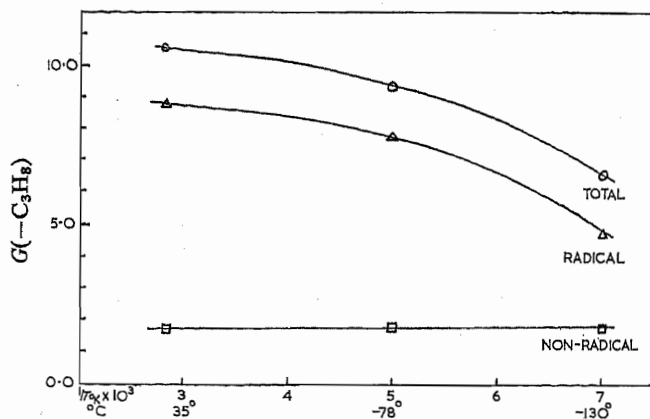


FIG. 2.—Total decomposition yields for radical, non-radical and total products against reciprocal temperature ( $1/T$ ) for liquid propane  $\gamma$ -irradiated to 1.2 Mrad.

the butadiene results show greater deviation. Our lower yield of scavenged methane is found both with oxygen and butadiene as scavengers.

Fig. 1 plots the yield of several radical products ( $\Delta G$ ) against reciprocal temperature ( $1/T$ ) for liquid propane. Between 35 and  $-78^\circ\text{C}$  the total radical yield is nearly constant and between  $-78$  and  $-130^\circ\text{C}$  it decreases. The total number of parent molecules reacting, as given by  $G(-\text{C}_3\text{H}_8)$  in fig. 2, shows similar behaviour. Between 35 and  $-78^\circ\text{C}$ , combination products involving *n*-propyl radicals (2-methylpentane, *n*-hexane and *n*-pentane) increase while the combination product involving only isopropyl radicals (2,3-dimethylbutane) decreases steadily. Propylene also decreases through this range.

Fig. 3 and 4 summarize dose dependence studies in the liquid phase at  $-130^{\circ}\text{C}$  and  $35^{\circ}\text{C}$ . Scavengeable propylene decreases sharply with dose in the  $-130^{\circ}\text{C}$  liquid and slowly with dose in the  $35^{\circ}\text{C}$  liquid. Hexanes remain constant in the  $-130^{\circ}\text{C}$  liquid and show a gradual net decrease in the  $35^{\circ}\text{C}$  liquid. The distribution of the various hexanes does not vary in either case.

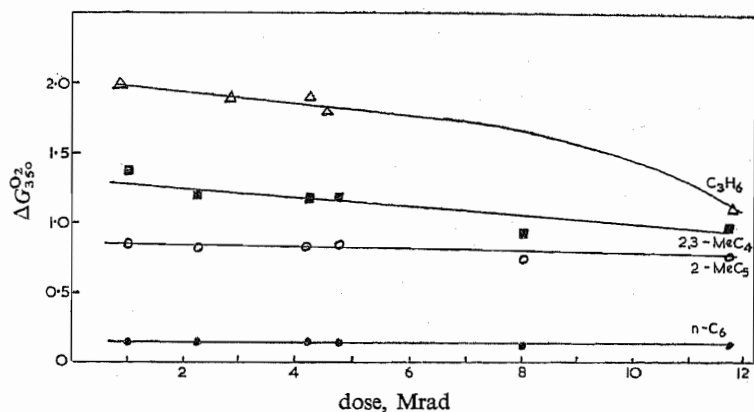


FIG. 3.—Radiation dose dependence of liquid propane radiolysis products with propyl radical precursors at  $35^{\circ}\text{C}$ .

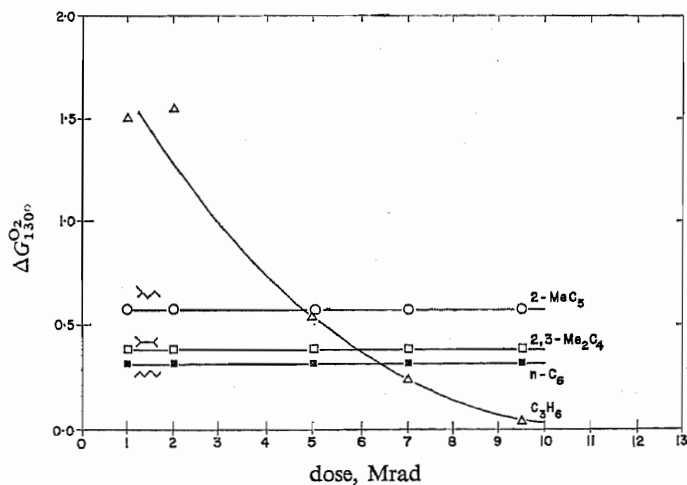


FIG. 4.—Radiation dose dependence of liquid propane radiolysis products with propyl radical precursors at  $-130^{\circ}\text{C}$ .

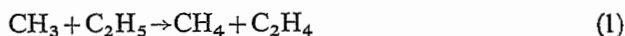
## DISCUSSION

Only radical reactions and radical contributions to products will be discussed. We consider that all oxygen scavengeable yields arise from thermal radical reactions.

### CALCULATION OF SCAVENGEABLE PRODUCT YIELDS

In irradiated propane the radicals to be considered are methyl, ethyl, *n*-propyl, isopropyl, and hydrogen atoms. A considerable amount is known about the types

and rates of simple alkyl radical reactions in the gas phase. Therefore one should be able to account for scavengeable product yields on a quantitative basis in terms of disproportionation and combination. At room temperature hydrogen atoms will react by abstraction from propane since the activation energy for this reaction is about 5 kcal mole<sup>-1</sup> for secondary hydrogens and since the steady-state radical concentration is low. The alkyl radicals, with the possible exception of part of the methyl radicals, will react by disproportionation and combination. The fact that essentially all of the C<sub>4</sub>-C<sub>6</sub> products in irradiated propane in both gas and liquid phases are scavengeable implies that they are produced by radical combination reactions. If the disproportionation to combination ratios (D/C) are known for the various radical pairs one can calculate the disproportionation contributions to the lower molecular weight products (C<sub>1</sub>-C<sub>3</sub>). In propane the following two reactions must also be considered:



The yields of these reactions cannot be independently determined from the experimental data and hence are taken to give best agreement with experiment.

The four scavengeable product yields to be calculated are methane, ethane, ethylene and propylene. The calculated values should agree with experimental

TABLE 2.—CALCULATED AND OBSERVED SCAVENGEABLE PRODUCT YIELDS ( $\Delta G$ ) IN IRRADIATED PROPANE

phase and temperature	calc. or expt.	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>
gas, 35°C	expt. <sup>a</sup>	·50	·20	·60	1·14
	calc.	·45	·23	·60	1·22
liquid, 35°C	expt.	·44	·15	·13	2·0
	calc. <sup>b</sup>	·42	·17	·13	2·0
liquid, -78°C	expt.	·19	·09	·18	1·6
	calc. <sup>c</sup>	·19	·09	·18	1·6
liquid, -130°C	expt.	·22	·14	·22	1·6
	calc. <sup>d</sup>	·21	·15	·22	1·6

<sup>a</sup> ref. (7); <sup>b</sup> D/C = 1·3 × gas phase value in ref. (12); <sup>c</sup> D/C = 1·5 × gas phase values in ref. (12); <sup>d</sup> D/C = 1·7 × gas phase values in ref. (12).

values if the interpretation is correct. The ethane yield can always be fit with the assumed yield of reaction (2). The methane and ethylene yields are dependent on the disproportionation contributions from the C<sub>4</sub>-C<sub>6</sub> products and on the assumed yield of reaction (1); thus either the methane or ethylene yield can always be fitted but the other provides a test of the assumptions involved. The propylene yield depends entirely on disproportionation contributions and provides a direct test of the D/C ratios used.

Part of the methyl radicals may react by abstraction with propane to form methane. This will complicate interpretation and calculation of the scavengeable methane yield. However, the calculated methane and ethylene yields can both be fitted to experiment with one parameter, the yield of reaction (1). If methyl radical abstraction is included then the calculated methane and ethylene yields can always be made to fit experiment because there are two parameters. We cannot conclude that methyl radical abstraction is unimportant, only that it is not necessary to include it as a principal reaction. This is also implied in the work of Bone, Sieck and Futrell.<sup>7</sup>

Our main discussion involves the effect of temperature and phase on D/C ratios in radiolytic systems. This is related mainly to the propylene yields and does not depend on possible complications introduced by methyl radical abstraction.

In the gas phase a comparison of calculated and experimental yields of disproportionation products based on the combination products and a set of D/C ratios has been made by Bone, Sieck and Futrell.<sup>7</sup> A set of D/C ratios all determined in one laboratory was used<sup>12</sup> and the agreement between experimental and calculated yields was good. Our own less extensive gas phase data do not give as good agreement

The same type of calculation has been performed on our liquid-phase data at three different temperatures. In no case was good agreement found between calculated and observed yields if the 25°C gas phase D/C ratios<sup>12</sup> were used. However, when all D/C ratios were increased by the same fraction to account for phase and temperature effects excellent agreement between the calculated and experimental values was found (see table 2).

#### PHASE EFFECTS

Table 1 shows that a change from gas to liquid phase decreases  $G(-C_3H_8)$ . This total decomposition yield drops from 12.1 to 10.4, or by 14 %. If one considers the radical yield apart from the total yield the drop is from 9.2 to 8.8 or 4 %. There appears to be a significant phase effect on the non-radical yields and little effect on the radical yields. The simplest interpretation is that the liquid state decreases the average excitation energy of the decomposing species due to partial collisional deactivation.

Published work on linear and branched alkane radiolysis yields few data with which to assess phase effects. Only in neopentane and in n-hexane can a comparison of  $G(-RH)$  be made for gas and liquid phases at the same temperature. Comparable data for scavenged systems was not found. In neopentane at 1.2 Mrad dose,  $G(-RH)$  decreased from gas (6.6) to liquid (5.9) by 11 %, but this is based on gas-phase data of one worker<sup>13</sup> and liquid-phase data of a different worker.<sup>14</sup> In n-hexane gas phase data are only available at high dose (30 Mrad);  $G(-RH) = 8.8$ .<sup>15</sup> This may be compared with liquid-phase data by the same worker at 30 Mrad (8.6)<sup>16</sup> or by a different worker at <1 Mrad (6.5);<sup>17</sup> in the latter case the decrease from gas to liquid is 26 %. The limited data available on alkane radiolysis are consistent with our detailed comparison of the phase effect at constant temperature in propane radiolysis.

A second phase effect is that D/C ratios are increased in the liquid phase. This is shown in table 2. The experimental and calculated scavengeable yields of propylene methane and ethylene in the 35°C liquid agree well if the gas phase D/C ratios at 35°C are all increased by a factor of 1.3. Dixon, Stefani and Szwarc<sup>18</sup> have studied phase effects on ethyl radical reactions and found that D/C was increased. Their experiments involved photolysis of azoethane in the gas phase and dissolved in iso-octane and in other more polar solvents. At 0°C, D/C in iso-octane was greater than in the gas phase by a factor of 1.36. This is nearly the same fractional increase as we observe for radicals in propane. From the limited data on this D/C increase with phase it appears to be an important effect which should not be neglected in radiolytic and photolytic systems.

Szwarc *et al.*<sup>18</sup> have suggested that disproportionation may be favoured more in the liquid phase due to (a) solvation of the unpaired electron end of the radical, or to (b) a lower volume of activation for the transition state for disproportionation than for the transition state for combination. (This latter statement implicitly assumes different transition states for disproportionation and combination). One

can also postulate that spatial configuration is more restrictive for disproportionation and that disproportionation would be enhanced in a liquid cage.

A third phase effect is indicated by examination of the isomeric hexane yields. In the liquid phase all products from combination of isopropyl radicals are considerably less compared to the gas phase yields than are products from n-propyl radical combination. One concludes that the  $G(\text{isopropyl})/G(\text{n-propyl})$  radical ratio is less in the liquid than in the gas. We have put this conclusion on a quantitative basis by considering disproportionation and combination reactions of all the radicals. In the gas phase at 35°C  $G(\text{isopropyl})/G(\text{n-propyl}) = 7.2$ ; in the liquid phase at 35°C  $G(\text{isopropyl})/G(\text{n-propyl}) = 4.0$ .

#### TEMPERATURE EFFECTS

Temperature will affect the relative rates of radical reactions having different activation energies. This should be evident in H abstraction from propane against H addition to product propylene. Fig. 2 shows that there is only a slight decrease of both total and radical  $G(-\text{C}_3\text{H}_8)$  from 35 to  $-78^\circ\text{C}$ , and a significant decrease from  $-78^\circ\text{C}$  to  $-130^\circ\text{C}$ . These changes are due to the relative importance of reactions (3) and (4). As the temperature is lowered the activation energy difference between reactions (3) and (4)



causes the rate constant ratio  $k_3/k_4$  to decrease and allows evaluation of the ratio. The concentration of propylene relative to propane at 1 Mrad dose is approximately  $3 \times 10^{-6}$ . When propylene competes effectively with propane for H atoms one less molecule of propane is removed;  $G(-\text{C}_3\text{H}_8)$  thus decreases.  $G(\text{C}_3\text{H}_6)$  must also decrease since the propyl radical formed by addition will most probably react with another propyl radical. Such a reaction could return a maximum of one propylene to the system for the two removed by H addition if  $D/C \gg 1$ . Since  $D/C \sim 1$  even less propylene is reformed. Therefore, the change in slope at  $-78^\circ\text{C}$  in fig. 2 gives an approximate value of  $3 \times 10^{-6}$  for the ratio  $k_3/k_4$  at  $-78^\circ\text{C}$ .

Activation energies for reactions (3) and (4) in the gas phase have been determined by Yang.<sup>19</sup> A value of  $k_3/k_4$  for  $3 \times 10^{-6}$  at  $-78^\circ\text{C}$  is calculated by using his values. The value of  $k_3/k_4$  at  $-78^\circ\text{C}$  calculated from our data is in good agreement with Yang's value. Thus, the H atom reaction rates for (3) and (4) are similar in gas and liquid phases.

Temperature also affects D/C ratios for radicals in both gas and liquid phases.<sup>18</sup> In the calculation given in table 2, in liquid propane between 35 and  $-78^\circ\text{C}$ , D/C increases by about 16 %, and between  $-78$  and  $-130^\circ\text{C}$ , D/C increases by another 15 %. The fact that D/C must increase with decreasing temperature to be consistent with the radical interpretation in irradiated propane is in good agreement with the 72 % increase over the same temperature range found for ethyl radicals generated by photolysis in iso-octane.<sup>18</sup> Gillis<sup>20</sup> has reported that D/C ratios for radicals in irradiated liquid methane at 112°K are higher than gas phase values; he does not separate phase and temperature effects, however.

A third temperature effect concerns the ratio of isopropyl to n-propyl radicals. At 35,  $-78$  and  $-130^\circ\text{C}$  the  $G(\text{isopropyl})/G(\text{n-propyl})$  ratios are 4.0, 1.4 and 1.4 respectively. The change between 35 and  $-78^\circ\text{C}$  is large. If one examines independent radiolysis data for hexane one finds the same trend; the 2-hexyl/1-hexyl radical ratio decreases with decreasing temperature.<sup>17, 21</sup> This effect cannot be

explained by H atom precursors to the propyl radical, but could be explained by a contribution from  $\text{CH}_3$  radical precursors to the isopropyl radical via abstraction. The proportion of abstraction would decrease at lower temperatures to produce a lower isopropyl/n-propyl ratio. In place of abstraction the methyl radicals would in part combine to increase the ethane yield. This is indeed observed. Ionic precursors may also be involved.

#### DOSE EFFECTS

In the gas phase radiolysis of alkanes, yields of both alkenes and dimers decrease at high dose.<sup>8</sup> This dose effect has previously been attributed to scavenging of reactive intermediates by alkene products. Back<sup>11</sup> has suggested that it is H atoms that are scavenged by the alkene to form excited propyl radicals, while Futrell, Bone, and Sieck<sup>7</sup> have concluded that in propane  $\text{C}_3\text{H}_7^+$  and  $\text{C}_3\text{H}_8^+$  must also be scavenged by alkene products to form propyl radicals. In the absence of alkene scavenging,  $\text{C}_3\text{H}_7^+$  and  $\text{C}_3\text{H}_8^+$  are precursors to H atoms, so the net experimental result is the same whether H atoms or these ions are scavenged. Alkene is lost by the scavenging reaction and although some alkene is reformed by subsequent disproportionation there is a net loss of alkene. The loss of dimer is attributed to a higher D/C ratio for excited radicals produced in the scavenging reaction.

The above explanation is qualitatively consistent with the gas phase experimental results. If we examine the liquid phase data in fig. 3 and 4, however, we see that the liquid phase effects are not explained at the lower temperature. Fig. 3 shows liquid propane at 35°C; the decrease of propylene and of hexanes above 5 Mrad can be explained in the same way as in the gas phase. However, the dose data in fig. 4 at -130°C is not explicable in terms of H atom addition to propylene. At -130°C the rate of reaction (4) greatly exceeds that of reaction (3) and even at 1 Mrad all H atoms add to propylene. At higher doses this reaction will be unchanged and no dose effect is predicted. The specific dose effect observed for propylene can perhaps be attributed to  $\text{C}_3\text{H}_6$  involvement in ion neutralization.

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